Sol–Gel Synthesis and Simultaneous Oxidation of $Ln_2Ba_2Cu_2Ti_2O_{11-\delta}$

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The synthesis of several substituted and unsubstituted derivatives of the series of layered perovskites $Ln_2Ba_2Cu_2Ti_2O_{11}$ by a sol–gel method is reported. Reduced synthesis temperatures were attained for La, Nd (750°C), and Eu (900°C) derivatives, whereas Tb derivatives could not be obtained by this method. The products were characterized by small particle sizes of 30–100 nm (compared to ~ 800 nm for samples prepared by the classical ceramic method). Furthermore, *in situ* oxidation of the samples took place leading to oxidized products, such as $La_2Ba_2Cu_{2.15}Ti_2O_{11}$, which earlier could have been obtained only by high oxygen pressure (5 kbar) annealing. © 1998 Academic Press

Key Words: copper–titanium oxides; layered cuprates; sol–gel; oxidation; soft chemistry.

INTRODUCTION

The series of oxides of formula $Ln_2Ba_2Cu_2Ti_2O_{11}$ ($Ln =$ La–Tb) belong to an emerging class of layered cuprates where the bidimensionality results from the alternation of different perovskite blocks. This is in contrast to other layered cuprates formed by perovskite/rock-salt (or fluorite) intergrowths. For the title compounds, a wise choice of cationic composition in combination with the induction of oxygen vacancies leads to the isolation of $Cu–O_2$ planes within the framework of an "all-perovskite" structure (Fig. 1).

Several members of this series have been reported and structurally characterized, among them the Lanthanum (1–4), Neodimium (1–4), Europium (1–4), Gadolinium (5), and Terbium (3, 6) derivatives and also derivatives containing two different lanthanides (7). We have also studied and reported recently detailed structural characterization of several derivatives by means of X-ray, electron, and neutron diffraction and by HRTEM. Finally, we have carried out several experiments of cation substitution and doping (both at ambient pressure and at high O_2 pressures) in an attempt to induce superconductivity in these phases. The oxidation

of these layered perovskites has proven a very difficult task. As a matter of fact, aliovalent cationic substitutions are systematically accompanied by a proportional change in the oxygen content resulting in an effectively unchanged formal oxidation state for the solid. Only after annealing under 5 Kbar of oxygen in autoclaves has it been possible to fill the additional oxygen vacancies induced by aliovalent substitutions, thus effectively doping these oxides. Furthermore, this has only been possible in the case of the lanthanum derivative, which is the one with the longest $Cu–O_{eq}$ bond lengths of all the series (1.973(5) (2)). Not surprisingly, the doped oxide does not present superconductivity. For the doping of other derivatives with shorter distances and therefore with higher probabilities of becoming superconductors, higher oxygen pressures should be used. We have also performed alternative electrochemical doping (13b).

Sol–gel synthesis of oxides and, in general, soft chemistry routes to these materials are known to yield products of smaller particle size at lower reaction temperatures. This behavior has been found in many publications relating to a number of different materials. On the other hand, an aspect not so widely known about sol–gel syntheses relates to the highly oxidizing conditions attained during these syntheses, especially when pyrolisis of nitrate-containing precursors is involved. As an example, different reports on the synthesis of $BaCuO_{2+\delta}$ show that starting from peroxides and/or nitrates or acetates it is possible to obtain high Cu(III) contents in this oxide (large values of δ) (8, 9). When the synthesis takes place from a sol–gel precursor containing nitrates, a value of δ indicating 100% Cu(III) ($\delta = 0.5$) is obtained (8).

We report here our recent results dealing with the synthesis and *in situ* oxidation by means of sol–gel methods of the series of layered perovskites $Ln_2Ba_2Cu_2Ti_2O_{11}$ ($Ln =$ La, Nd, Eu, Tb) for which oxidation has proven so difficult by means of traditional solid-state and annealing methods.

EXPERIMENTAL

Synthesis

The synthesis of $Ln_2Ba_2Cu_2Ti_2O_{11-\delta}$ and some derivatives of this oxides with cationic substitution was carried out

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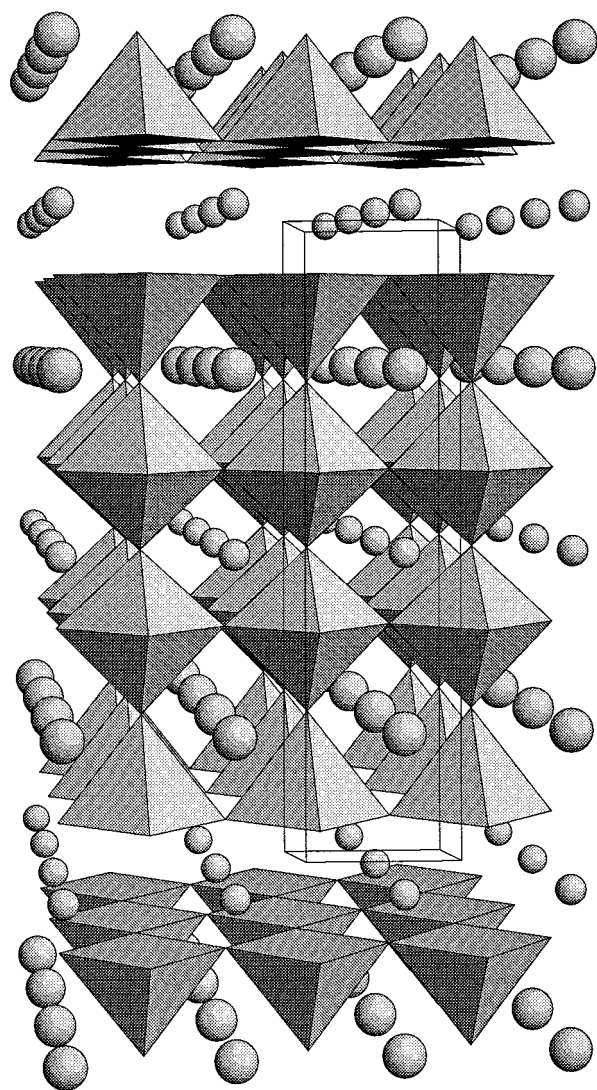
FIG. 1. Structure of the family of oxides $Ln_2Ba_2Cu_2Ti_2O_{11}$. Copper and titanium occupy the square–pyramidal and octahedral positions, respectively, and lanthanide is represented by small circles and barium by larger ones.

by means of a sol–gel process. For the syntheses of samples with nominal compositions $Ln_2Ba_2Cu_2Ti_2O_{11-\delta}$ (Ln = La, Nd, Eu, Tb) and $Ln_2Ba_2Cu_{2.15}Ti_{1.85}O_{11-\delta}$ (Ln = La, Nd, Eu), stoichiometric amounts (to yield ca. 2 g of final product) of lanthanide nitrate (Aldrich, $Ln(NO_3)_3 \cdot nH_2O$ Ln = La, Nd, Eu, Tb, n = 6 for Ln = La, Nd and n = 5 for Ln = Eu, Tb) copper nitrate (Merck, $Cu(NO_3)_2 \cdot 3H_2O$ and tetrapropylorthotitanate (Fluka, $Ti(C_3H_7O)_4$) were dissolved in ca. 50 ml of 1-propanol to yield a blue solution (solution 1). Independently, $BaCO_3$ was dissolved in ca. 20 ml of acetic acid 17 M (solution 2). Solutions 1 and 2 were mixed and a white gel formed; the resulting mixed suspension was evaporated to dryness and a blue precursor

was obtained. For the synthesis of samples of nominal compositions $Ln_2Ba_2Cu_2Ti_{1.7}Al_{0.3}O_{11-\delta}$ and $Ln_2Ba_{1.7}K_x$ $Cu_2Ti_2O_{11-\delta}$, $Al(NO_3)_3$, and K_2CO_3, respectively, were also used. In the case of aluminum, the nitrate was dissolved in solution 1, whereas in the case of potassium, the carbonate was dissolved in solution 2. In order to avoid violent pyrolisis, the precursor was then heated very slowly (50°C/h) to 225°C and kept at this temperature, where a loss of nitrogen oxides was detected (caution: hood or gas exhaust must be used). Analogous treatments to avoid pyrolisis have been described for example in the case of $YBa_2Cu_4O_8$ (10) (caution: if heating is too fast, the quick development of the exothermic pyrolisis process causes a vigorous production of gases and projection of solid particles). After treatment, the precursor was heated at the same rate to the temperature of the reaction. This temperature was typically 750°C and the reaction time 72 h. In the case of samples containing lanthanum, a study of the reaction at different temperatures between 500 and 750°C was also made. In the case of samples containing europium, the final temperature must be increased to 900°C to obtain pure products. All thermal treatments were carried out under flowing oxygen.

Elemental Analysis

Elemental analysis was performed on all the products to detect possible impurities containing C, N, or H, which could have remained in the samples after calcination at the synthesis temperature. A Carlo Erba CHN EA 1108 analyzer with a maximum combustion temperature of 1800 °C was used.

Chemical Analysis

Analysis of potassium was considered necessary since it is the only cation used that forms compounds with relatively high volatility at the temperature used. The amount of potassium present in the corresponding sample was analyzed by atomic absorption (AA) using a Perkin–Elmer 2100 analyzer. Each sample was prepared twice for analyses to obtain two independent results in every case. The preparation was made by dissolving ca. 50 mg of sample in hot HNO_3 and then adding water to obtain 250 ml of solution.

The oxidation state of copper in the samples, and therefore the oxygen content, was analyzed by iodometric titration, following the procedure described by Nazzal *et al.* (11), and by using ca. 30 mg of sample in each of the two titrations made for each compound.

Electron Diffraction

Electron diffraction was performed with a JEOL JEM-1210 microscope operating at 120 kV with a double-tilt analytical GATHAN 646 sample holder. Samples were

dispersed in *n*-butanol and a drop of this dispersion was deposited on a carbon-coated holey film supported on an either aluminum or copper grid.

X-Ray Diffraction

The progress of the reaction was followed by X-ray powder diffractometry. X-ray powder diffraction patterns were obtained using $CuK\alpha$ radiation with a Siemens D-500 diffractometer. Routine measurements were made between $2\theta = 5–60°$, with a step of $0.05°$ and 3 s counting time per step.

Magnetic Measurements

Magnetic susceptibility data were collected on a Quantum Design SQUID magnetometer. All samples were measured at 5 K with an applied field of 10 G to detect any possible diamagnetic signal, which would indicate superconducting properties. In the case of the oxide $La_2Ba_2Cu_2Ti_2O_{11.2}$, where there is no magnetic contribution due to the lanthanide ion, the magnetic susceptibility was measured at temperatures ranging from 5 to 300 K with an applied field of 10000 G in order to compare with $La_2Ba_2Cu_2Ti_2O_{11-\delta}$ synthesized by the ceramic method (3).

Resistivity Measurements

Resistivity values for $Ln_2Ba_2Cu_2Ti_2O_{11-\delta}$ were obtained by using the Van der Pauw method (12) on four contact resistance measurements and were compared with those of the corresponding oxides synthesized by the ceramic method and measured in the same conditions (13). The contacts were made with silver paint and copper wires on sintered pellets of each sample, and the measurements were performed with a Hewlett Packard 3457A multimeter (which allows one to apply intensities between 100 nA and 1 mA). The sintering process was carried out under flowing oxygen for 15 h at $750°C$. The measurements were performed both at room temperature and at 77 K. In some cases, where resistance values obtained were larger than $500 k\Omega$, due to saturation of the multimeter, approximate measurements were made by using only two contacts.

RESULTS AND DISCUSSION

The synthetic procedure used to prepare $Ln_2Ba_2Cu_2Ti_2O_{11-\delta}$ by a sol–gel method is similar to the one we reported earlier to synthesize La_2CuTiO_6 (14). However, in the present case, the presence of acetate ligands, with great ability to act as bidentate and displace alkoxide ligands, leads to the formation of a gel (15–18). Another important difference is that in the case of La_2CuTiO_6 the precursor
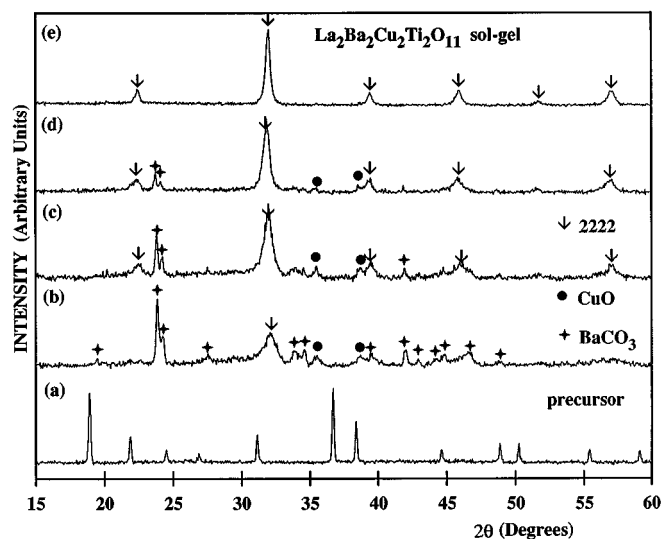

FIG. 2. X-ray powder diffraction patterns corresponding to the synthesis of $La_2Ba_2Cu_2Ti_2O_{11}$: (a) the initial sol–gel precursor, (b) after treatment at $500°C$ for 48 h, (c) with additional treatments at 550, 600, and $650°C$ also for 48 h each, (d) after an additional treatment at $700°C$ for 48 h, and (e) after a final treatment at $750°C$ for 48 h.

was amorphous, whereas in the case of $Ln_2Ba_2Cu_2Ti_2O_{11-\delta}$ it is crystalline (see Fig. 2a). The compounds present in this precursor product could not be identified with the JCPDS standards, but we believe it must contain a mixture of mixed acetates of the metals *Ln*, Ba, Cu and Ti.

In the case of $Ln_2Ba_2Cu_2Ti_2O_{11-\delta}$, the precursor was heated successively at 500, 550, 600, 650, 700, and $750°C$ for periods of 48 h each. The X-ray powder diffraction patterns are shown in Fig. 2 together with that of the precursor product. In the case of the sample heated at $500°C$, $BaCO_3$ is the major phase but the sample contains also CuO and already a small amount of $La_2Ba_2Cu_2Ti_2O_{11-\delta}$. With treatments (all for 72 h) at 550, 600, and $650°C$ the X-ray powder diffraction pattern does not change too much and the same phases are present, but the relative amount of $La_2Ba_2Cu_2Ti_2O_{11-\delta}$ increases with the temperature, and the amount to $BaCO_3$ decreases at the same time. After treatment at $700°C$, only a small amont of $BaCO_3$ is observed, and at $750°C$, $La_2Ba_2Cu_2Ti_2O_{11-\delta}$ is obtained as a pure phase. In some cases, a very small amount of CuO as an impurity is difficult to remove, similar to what happened in the sol–gel synthesis of the related oxide La_2CuTiO_6 (14). Thus, the sol–gel method allows a very important effective decreases in the temperature of synthesis of this oxide, because with the ceramic method it cannot be obtained at temperatures lower than $1100°C$ (3).

The synthesis at $750°C$ has also been tried for $Ln_2Ba_2Cu_2Ti_2O_{11-\delta}$ (*Ln* = Nd, Eu, and Tb) and the X-ray powder diffraction patterns of the products are shown in Fig. 3. The first remarkable result is that sol–gel synthesis of
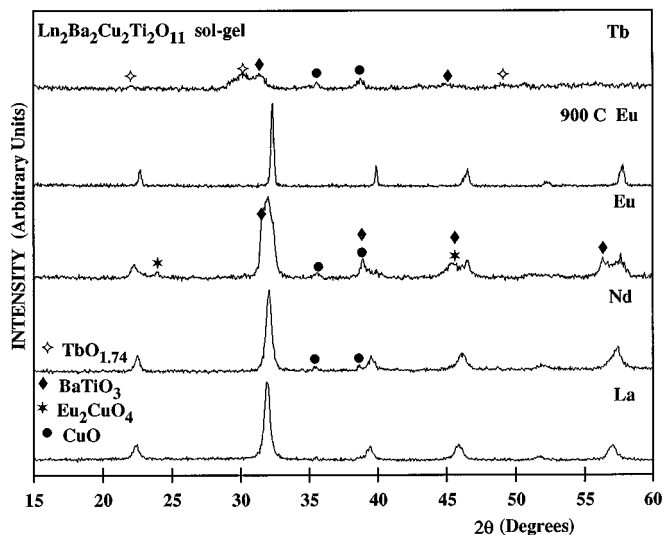
FIG. 3. X-ray powder diffraction patterns of the product of the synthesis of samples with nominal composition $Ln_2Ba_2Cu_2Ti_2O_{11-\delta}$ ($Ln =$ La, Nd, Eu, Tb) at 750°C from a sol–gel precursor. In the case of $Ln =$ La and Nd, $Ln_2Ba_2Cu_2Ti_2O_{11-\delta}$ is obtained as a pure phase, with the exception of a small amount of CaO as an impurity in some cases. For $Ln =$ Eu, $BaTiO_3$ and Eu_2CuO_4 are present in the reaction product, but they disappear after heating at 900°C. In the case of $Ln =$ Tb, a mixture of oxides is obtained, including Tb(IV) containing oxides. The oxidation of terbium is due to the highly oxidizing synthetic conditions.

$Ln_2Ba_2Cu_2Ti_2O_{11-\delta}$ cannot be attained for $Ln =$ Tb and a mixture of $TbO_{1.81}$, $BaTiO_3$, and CuO is obtained as a result of the reaction (see Fig. 3). We believe that this is due to the stability of terbium on its $+4$ oxidation state. This is the reason precluding the synthesis of $TbBa_2Cu_3O_{7-\delta}$ (19, 20). In our case, this factor is also favored by the fact that the synthesis is carried out under very oxidizing conditions (under oxygen flow and with production of nitrogen oxides). On the other hand, the europium derivative cannot be obtained as a pure phase at 750°C, and further heating up to 900°C is needed in order to eliminate $BaTiO_3$ and Eu_2CuO_4 impurities (see Fig. 3). This process also improves the crystallinity of the sample and narrower diffraction peaks are observed. We believe that the need of a higher temperature for the synthesis of the europium derivative is related to the fact that the structure of these oxides becomes less stable with the decreasing radius of the lanthanide and therefore more drastic synthesis conditions are needed.

Oxides with cationic substitution have also been synthesized in order to obtain doped derivatives of $Ln_2Ba_2Cu_2Ti_2O_{11-\delta}$. Samples of nominal composition $Ln_2Ba_2Cu_2Ti_{1.7}Al_{0.3}O_{11-\delta}$, $Ln_2Ba_{1.7}K_xCu_2Ti_2O_{11-\delta}$, and $Ln_2Ba_2Cu_{2.15}Ti_{1.85}O_{11-\delta}$ ($Ln =$ La, Nd, Eu) were synthesized. In the case of aluminum-substituted samples, no pure products were obtained at 750°C, although the substitution is possible by using the ceramic method (13a). One
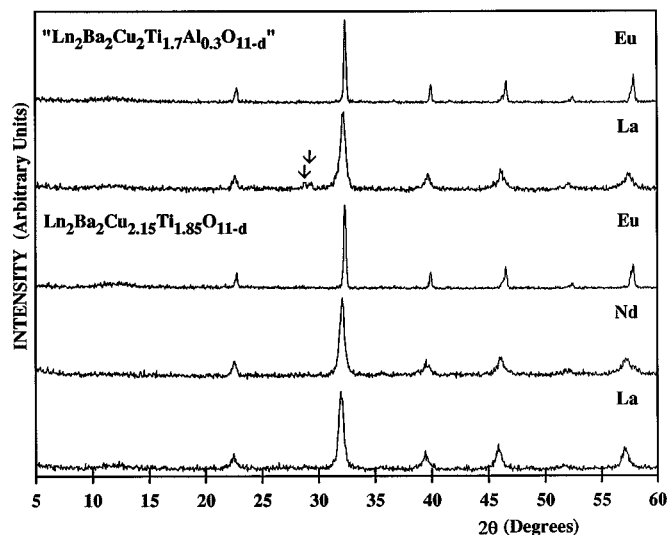

FIG. 4. X-ray powder diffraction patterns corresponding to $Ln_2Ba_2Cu_{2.15}Ti_{1.85}O_{11-\delta}$ ($Ln =$ La, Nd, Eu), $Eu_2Ba_2Cu_2Ti_{1.7}Al_{0.3}O_{11-\delta}$, and the sample of nominal composition $La_2Ba_2Cu_2Ti_{1.7}Al_{0.3}O_{11-\delta}$, where some impurities can be observed. The synthesis was at 750°C except for the Eu-containing samples, where the temperature was 900°C.

possible explanation for this behavior would be the segragation of aluminum from the reaction mixture in any step of the synthetic procedure. On the other hand, copper- and potassium-substituted samples yielded pure products (see Fig. 4 and 5). For $Eu_2Ba_{1.7}K_xCu_2Ti_2O_{11-\delta}$ and $Eu_2Ba_2Cu_{2.15}Ti_{1.85}O_{11-\delta}$, the synthesis temperature had to be raised to 900°C to obtain pure products as in the case
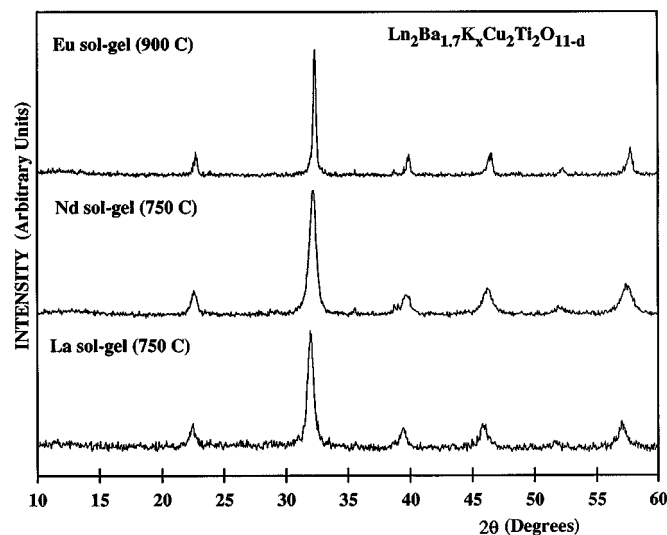

FIG. 5. X-ray powder diffraction patterns corresponding to $Ln_2Ba_{1.7}K_xCu_2Ti_2O_{11-\delta}$ ($Ln =$ La, Nd, Eu) prepared by heating the corresponding sol–gel precursor for 72 h at 750°C for $Ln =$ La, Nd, Eu and with an additional treatment at 900°C (48 h) for $Ln =$ Eu.

of the unsubstituted sample, this increased temperature also led to the disappearance of the impurity peaks in $Eu_2Ba_2Cu_2Ti_{1.7}Al_{0.3}O_{11-\delta}$, as can be seen in Fig. 4. An additional problem was encountered in the synthesis of $Ln_2Ba_{1.7}K_xCu_2Ti_2O_{11-\delta}$, related to the loss of potassium from the reaction mixture upon heating due to volatilization; this problem also appeared in the case of samples of the same composition synthesized by the ceramic method and is difficult to avoid even with the use of an excess of potassium in the starting stoichiometric mixture (13a). In fact, the analyses of the potassium content yield values very similar to those of the ceramic-synthesized samples and indicates a cationic defect in the barium positions of the structure. Thus, instead of the expected nominal composition $Ln_2Ba_{1.7}K_{0.3}Cu_2Ti_2O_{11-\delta}$, the mean values obtained are $La_2Ba_{1.7}K_{0.04}Cu_2Ti_2O_{11-\delta}$, $Nd_2Ba_{1.7}K_{0.14}Cu_2Ti_2O_{11-\delta}$, and $Eu_2Ba_{1.7}K_{0.14}Cu_2Ti_2O_{11-\delta}$.

The particle size of the products has been measured by transmission electron microscopy, and is found to be mainly between 30 and 100 nm (see Figs 6a and 6b). Similar particle sizes have been reported by different authors in similar syntheses of diverse oxides, such as $YBa_2Cu_3O_{7-\delta}$ (21), and oxides containing titanium and calcium or barium (22–24). The sol–gel method allows therefore the obtention of oxides belonging to the family $Ln_2Ba_2Cu_2Ti_2O_{11-\delta}$, with a particle size considerably smaller than that obtained by the ceramic method (around 800 nm). Given the small particle size, electron diffraction experiments led only to powder-like patterns (see Fig. 6c). Rings corresponding to the typical d values of a perovskite structure are observed in these patterns; however, it is neither possible to confirm nor to discard the presence of superstructure reflections in these patterns due to the proximity of the expected d values, which precludes an unambiguous indexing of the rings. However, in some cases, it is possible to find some larger particles yielding single-crystal electron diffraction patterns. In these cases, superstructure reflections are observed but only as diffuse spots (see Fig. 7). This indicates an important degree of disorder in the structure when compared to the compounds synthesized by the ceramic method. On the other hand, in the case of lanthanum derivative, and due to the more similar sizes of lanthanum and barium, the degree of disorder is probably higher, similar to what occurs in the sample obtained by the ceramic method (4).

Elemental analyses of the samples synthesized at 750°C showed that they contain residual H, N, or C. The amounts depend on the sample, but, in general, the hydrogen and nitrogen contents are always smaller than 0.01 and 0.25%, respectively, being smaller in the case of neodymium and europium unsubstituted samples than for the rest of them. The carbon content is typically $<0.05\%$ in the unsubstituted samples and $<0.2\%$ in the substituted samples. In the case of europium-containing samples, all these residues disappear after treatment at 900°C.

The fact that the samples contained these minor residues due to the incomplete calcination of the precursor made advisable the use of iodometry instead of thermogravimetry to determine the oxidation state of copper in the samples. The results obtained for all pure phases are shown in Table 1. The most remarkable result is that two of the La-containing samples contain approximately 20% Cu(III). All the other samples seem not to contain Cu(III), or in any case the values obtained are too close to experimental error. Considering the difficulty in doping the $Ln_2Ba_2Cu_2Ti_2O_{11}$ oxides (13), the fact that with the use of an alternative synthetic method we are able to partially overcome this problem reinforces the importance of the reaction path and synthetic conditions in the products of the reactions. This is not the only example of this kind of behavior. The oxide $BaCuO_{2.5}$ can also be synthesized with 100% Cu(III) at 650°C by using a sol–gel nitrate-based method, as we have stated before (8, 9), whereas by the ceramic method it can only be attained under high oxygen pressure (400°C) (25). In the family $Ln_2Ba_2Cu_2Ti_2O_{11}$, the only doped derivative obtained by the ceramic method is $Ln_2Ba_2Cu_{2.15}Ti_{1.85}O_{11}$, but it must be oxidized after the synthesis also under high oxygen pressure (3500–5000 atm) (13a).

Our results confirm therefore the possibility of obtaining an by the sol–gel method at ambient pressure compounds in unusually high oxidation states which would otherwise need high pressures of oxygen to be obtained.

The magnetic measurements performed at 5 K in all samples indicate that none of them present superconducting properties, since even the doped samples show paramagnetic behavior. This is consistent with the fact that the lanthanum-doped sample prepared by the ceramic method and oxidized under high oxygen pressure is also paramagnetic (13). We believe this is a consequence of two factors: first, the degree of disorder present in the lanthanum samples (2, 4) and second, but more important, the $Cu–O_{eq}$ in plane distance, which in the case of the La derivative is probably too long to lead to superconducting properties. Transport measurements show that resistivity at low temperature is always higher than at room temperature, thus indicating semiconducting-like behavior for all samples.

The magnetic susceptibility of $La_2Ba_2Cu_2Ti_2O_{11.2}$ obtained via sol–gel was measured in the temperature range between 5 and 300 K, and the result was compared with that of $La_2Ba_2Cu_2Ti_2O_{11}$ obtained by the ceramic method (3). The plots of the effective magnetic moments per copper atom for both samples are shown in Fig. 8. The sol–gel synthesized sample presents an effective magnetic moment substantially lower than that of the ceramic synthesized sample at all temperatures. The presence of a large proportion of copper as Cu(III) in the sol–gel sample may account for this notable change in the magnetic properties. Two possible situations may be considered. A 20% quantity of diamagnetic Cu(III) would lower the effective magnetic
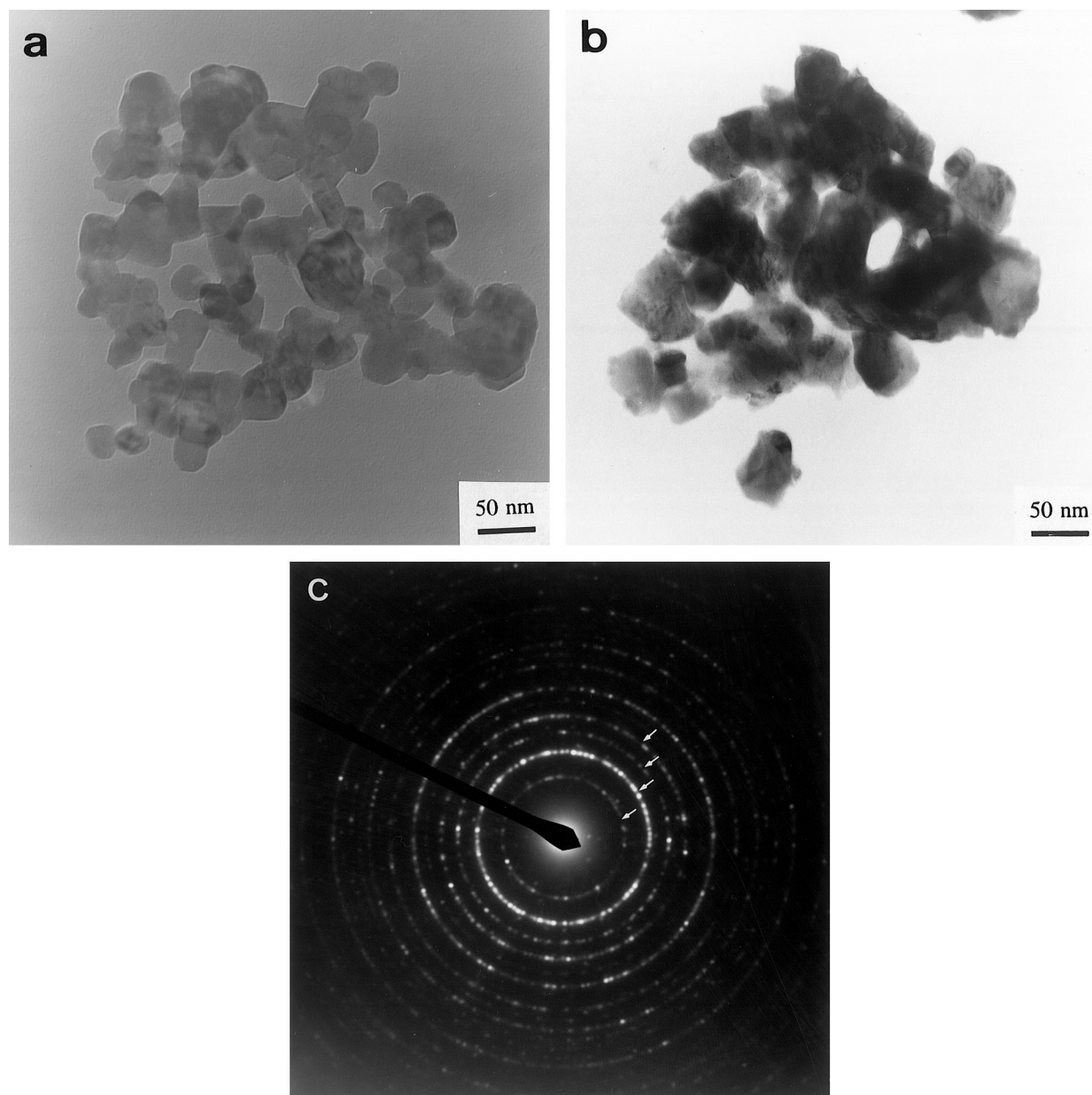
FIG. 6. Transmission electron microscopy images corresponding to $Ln_2Ba_2Cu_2Ti_2O_{11-\delta}$ ((a) Ln = La, (b) Ln = Eu) synthesized from the corresponding sol–gel precursor, where particle size can be seen (30–100 nm). (c) Electron diffraction pattern corresponding to an aggregate of particles of $Ln_2Ba_2Cu_2Ti_2O_{11-\delta}$. Some rings corresponding to typical distances of perovskite reflections are marked: $[100]_p$, $[110]_p$, $[111]_p$, and $[200]_p$ (ordered from smaller to greater reciprocal distance and corresponding respectively to real distances: 3.95, 2.82, 2.31, and 2.01 Å).

moment from approximately 1.0 to 0.75 μ_B at room temperature if it does not exert any influence in the antiferromagnetic exchange among Cu(II) ions. That would correspond to a Cu(III) clustering within the copper–oxygen network. On the other hand, if Cu(III) is located randomly within the network, we would expect a change due to the zero magnetic moment of Cu(III) (which would lower the moment), plus the partial breaking of the exchange among Cu(II) (which would raise the effective magnetic moment). In this case, therefore the effect would be a balance between two

opposite sign changes, which makes us predict a smaller change than in the first case.

Indeed the experimental values show that the differences between the ceramic and sol–gel samples are more consistent with the changes expected if we observe only the lowering of Cu(III) magnetic moment without any disruption of the Cu(II)–O–Cu(II) exchange, favoring the idea that the Cu(III) formed is clustered in particular zones of the network. However, the scheme may not be so simple, since the different slope of μ_{eff} vs T for both samples shows that
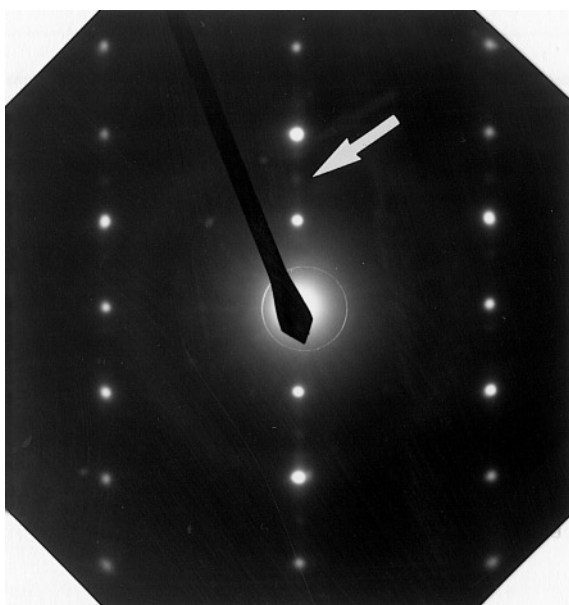
FIG. 7. Electron diffraction pattern corresponding to zone axis $[210]_p$ of a small crystal of $Nd_2Ba_2Cu_2Ti_2O_{11-\delta}$ (sol–gel). Although they are weak and diffuse, superstructure spots ($a_p \times a_p \times 4a_p$) can be observed.
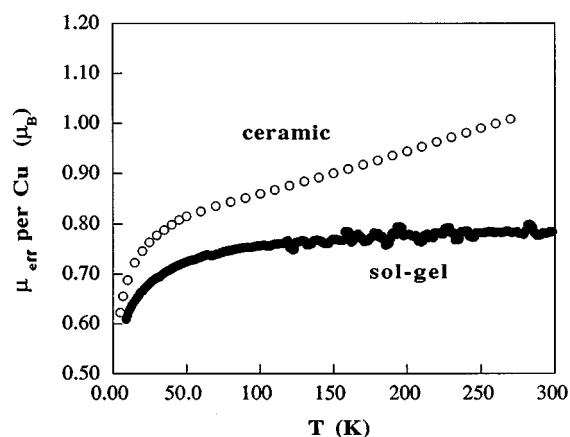

FIG. 8. Plots of the effective magnetic moment per copper atom corresponding to $La_2Ba_2Cu_2Ti_2O_{11-\delta}$ prepared both with the ceramic method at (1100°C for 2 days (3) and form the sol–gel precursor at 750°C. The magnetic moment is clearly lower in the sol–gel sample, which has been found iodometrically to contain 20% Cu(III).

the antiferromagnetic coupling among Cu(II) is indeed affected by the presence of Cu(III) or by its ordering.

CONCLUSIONS

We have been able to prepare several substituted and unsubstituted derivatives of the series $Ln_2Ba_2Cu_2Ti_2O_{11}$ (Ln = La, Nd, Eu) by a sol–gel procedure. As it could be expected, the particle size of the resulting product (~ 30–100 nm) is much smaller than that of similar ceramic

products (~ 800 nm). Also, the reaction temperature is substantially reduced although less so for the smallest Ln derivative. Surprisingly, the terbium derivative, which could be synthesized by the ceramic method, cannot be obtained via sol–gel; instead, oxidized terbium oxide products are obtained.

Finally, the sol–gel method has allowed the synthesis of oxidized products such as $La_2Ba_2Cu_2Ti_2O_{11.2}$ and $La_2Ba_2Cu_{2.15}Ti_{1.85}O_{11}$, which could be prepared earlier only by annealing under high oxygen pressure. This corroborates the importance of the strongly oxidizing conditions in sol–gel/pyrolisis methods and suggests the possibility of applying these methods for the synthesis of materials in unusually high oxidation states.

TABLE 1
Results of the Iodometric Analysis of the Oxidation State of Copper

Sample	% Cu(III) $\pm$ 2%	$\delta \pm 0.02$
$La_2Ba_2Cu_2Ti_2O_{11-\delta}$	20%	-0.20
$La_2Ba_{1.7}K_{0.04}Cu_2Ti_2O_{11-\delta}$	0%	$+0.28$
$La_2Ba_2Cu_{2.15}Ti_{1.85}O_{11-\delta}$	19%	-0.04
$Nd_2Ba_2Cu_2Ti_2O_{11-\delta}$	3%	-0.03
$Nd_2Ba_{1.7}K_{0.14}Cu_2Ti_2O_{11-\delta}$	3%	$+0.20$
$Nd_2Ba_2Cu_{2.15}Ti_{1.85}O_{11-\delta}$	4%	$+0.11$
$Eu_2Ba_2Cu_2Ti_2O_{11-\delta}$	3%	-0.03
$Eu_2Ba_{1.7}K_{0.14}Cu_2Ti_2O_{11-\delta}$	3%	$+0.20$
$Eu_2Ba_2Cu_{2.15}Ti_{1.85}O_{11-\delta}$	3%	$+0.12$
$Eu_2Ba_2Cu_2Ti_{1.7}Al_{0.3}O_{11-\delta}$	3%	$+0.13$

Note. Two of the La-containing samples contain approximately 20% Cu(III). All the other samples seem not to contain Cu(III), or in any case the values obtained are too close to experimental error.

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